

# How does a particle move in chemical kinetics?

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**Abstract.** We give a model of moving a big particle in chemical reactions. Direct and indirect photophoresis are explained on the basis of reactive forces.

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The case of a big particle, moving in chemically reacting gas, was considered. It was called chemojet motion and was found experimentally by chemists from Chemical faculty of Moscow State University [9]. A model of a chemical reaction on the surface of a body was created and a system of equations of motion was written and investigated [10-11]. We got an ideal cylindrical spiral trajectory in asymptotic when time tends to infinity. This justified qualitatively the result of experiment of European Cosmic Agency and of a group of scientists from Moscow State University. A step and a diameter of those cylindrical spirals were calculated in exact form. Also it gives the theory of positive and negative photophoresis and explains old experimental results, which were a subject of discussions for a long time. Consideration of photophoresis as an example of chemojet motion was proposed in [5-7].

The term photophoresis was proposed by Felix Ehrenhaft [1]. In his experiments dust, silver and copper particles in gases irradiated by light “strongly exhibited a tremendous lightnegative movement, although they ought to be most heated on the side toward the light, and would expect a movement away from the light” ([2]).

Movement towards light was called lightpositive or positive or direct photophoresis and away from it lightnegative or negative or indirect photophoresis.

“During the course of the experiment, the motion of the particle traced out a “spiral” path. However upon magnification of a given section of a given spiral, one saw a “spiral” path within the path of the larger spiral... In viewing these microphotographs, one had the distinct impression that something phenomenal was happening, but no definitive explanation for the observation was presented” [2].

Theory of photophoresis usually was considered in the framework of P.N.Lebedev irradiation pressure and heat effects. For a review see [3]. “A unilateral aerosol particle is affected by a photophoretic force and a radiation pressure force. The former is of a radiometric nature and is a result of gas molecules interacting with the non-uniformly heated particle surface” (this is the beginning of the paper [3]). “Depending upon the size and optical properties of material of a particle both irradiated and shadowed side of a particle can become more heated. That is why both negative and positive photophoresis could take place.” [4].

Our explanation is based on reactive forces. A particle evaporates molecules on irradiated side – this is the cause of positive photophoresis. This explanation is accepted in comet astronomy from 1950-is, when American astrophysicist F. Whipple suggested reactive forces connected with sublimation of comets. This idea was considered in [5-7]. Paper [8] can be direct experimental justification of this idea.

Negative photophoresis is considered on the basis of counter-reactive (or anti- reactive) forces. The light makes molecules to adhere: the force of momentum of adhered molecules is twice less than of elastically reflected ones. That is why additional pressure towards the source of light appears [5-7]. This is a simple explanation of negative photophoresis.

This movement have to be considered in the framework of more general class of movements – hemojet ones. It was discovered that big particles moves at any physical-chemical process [9] – the motion was called hemojet. Mathematical model of that motion was created in [10-11]. This model considered not only forces but torques as well: that is why instead of Newton second law we considered Euler equation for solids. Exact solution of the

equation showed spiral trajectories [10]. In [10] we constructed the model and got spiral paths for simplest case of spherical particles, and in [11] more general case of any convex particle was considered.

So we got a simple explanation both of negative photophoresis and Ehrenhaft spiral paths independently and in more general situation. This strongly justifies our general mathematical model [10 – 11]. On the other hand it gives explanation of mysterious Ehrenhaft helixes [1-2].

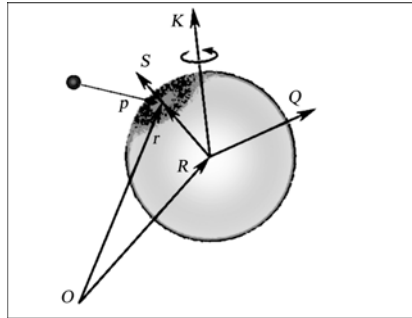
Ehrenhaft himself tried to explain it by introducing charges smaller than Electrons and/or by Dirac magnetic Monopoles. Dirac, Einstein and others denied both versions, but the experiments were not explained even roughly. Dirac objection was – magnetic charges can be obtained experimentally (if they exist) only for much higher energies. We see now that Ehrenhaft examined if not so fundamental appearance, but more close to reality, more often and much more useful for technical applications: it was an example of a spiral path of big (1/100 – 1/10000000 meters) particle in any physical or chemical process.

In [2] we have the following eloquent passage “Also curious is the fact that the winding shapes of some of this spirals in the microphotographs reminded me of the shapes described by Nicola Tesla with respect to Plate 48 in which Tesla wrote: “One of the streamers is wonderfully interesting on account of the curiously twisted and curve appearance. It is hard to conceive how a discharge can pass through the air in this way when there exists a strong tendency to make it take the shortest route”. The key word here is “discharges” as there is no any model for twisted discharges. It seems also that spirals from [10] explains strange forms of Northern Lights.

## 1. Model and a system of equations.

Here we follow [10].

A model can be described as follows. A particle is considered as a ball, which is determined by coordinates' of center of mass  $R$ , momentum  $Q$ , angular momentum  $K$ , and the unit vector  $S$  directed from a center of mass to the center of active zone (pic.1).



**pic 1.** A particle is considered as a ball, which is determined by coordinates' of center of mass  $R$ , momentum  $Q$ , angular momentum  $K$ , and the unit vector  $S$  directed from a center of mass to the center of active zone. A molecule has a momentum  $p$  and space coordinate  $r$ .

The forces that act on a particle are determined by collisions and a frequency of collisions has the usual in Kinetic theory expression:

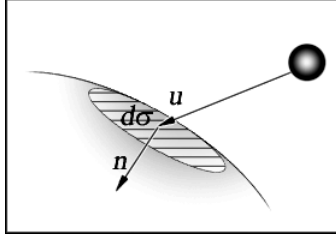
$$d\Omega = \sigma \cdot (u, n) \cdot \theta((u, n)) \cdot f(r, p) \cdot dr \cdot dp.$$

Here  $\sigma = \sigma(R, Q, r, p)$  – is a crosssection of collisions  $\{R, Q, S, K\} + \{r, p\} \rightarrow \dots$ , that for rigid spheres have the form

$$\sigma = \sigma(R, Q, r, p) = \delta(|r - R| - \rho),$$

$\theta(x) = \begin{cases} 1, & x > 0, \\ 0, & x \leq 0. \end{cases}$ ,  $\delta(x)$  is a Dirac  $\delta$ -function,  $u = \frac{p}{m} - \frac{Q}{M}$  is a relative velocity of a molecule and a ball,  $\rho$  is a

radius of a particle,  $n$  – is a unit vector orthogonal to a surface at the point  $r = R - \rho n$  (pic.2),  $f(r, p)$  is a distribution function of molecules over momentum  $p$  and space  $r$ .



**Pic.2.** A picture of a collision.  $u = \frac{p}{m} - \frac{Q}{M}$  – is a relative velocity of a molecule and a ball,  $n$  – is a unit vector orthogonal to a surface at the point  $r = R - \rho n$

We assume that some molecules are elastically reflected from the surface of the particle, and some of them adheres (the adherence here models chemical interaction).

We assume that the fraction of adhering particles at a point of the ball with the internal normal  $n$  is  $\beta = \beta(n)$ , and we put  $A = \int_{S_2} n \cdot \beta(n) dn$ . and orientation vector  $S = A/|A|$ . Dynamics of this vector is described by the equation  $\frac{dS}{dt} = \frac{1}{J} \cdot [K, S]$ , where  $\tilde{J}$  is a moment of inertia.

A system of equation can be written in the form

$$\begin{cases} \frac{dR}{dt} = \frac{Q}{M}, \\ \frac{dQ}{dt} = F_{chem} + F_{elast}, \\ \frac{dK}{dt} = M_{chem}, \\ \frac{dS}{dt} = \frac{1}{J} [K, S]. \end{cases} \quad (11)$$

The first equation is the definition of a velocity; the second is Newton law with two terms. The first one is connected with inelastic collisions and has the form

$$F_{chem} = \rho^2 \iint_{\mathbf{R}^3 \times \mathbf{S}^2} \beta(n, S) \{p - 2\mu(u, n)n\} (u, n) \theta((u, n)) f(R - \rho n, p) dn dp. \quad (12)$$

The second is determined by elastic collisions

$$F_{elast} = 2\mu\rho^2 \iint_{\mathbf{R}^3 \times \mathbf{S}^2} n(u, n)^2 \theta((u, n)) f(R - \rho n, p) dn dp. \quad (13)$$

The third equation describes changing of a moment  $\frac{dK}{dt}$  and connected only with inelastic collisions (in the case of a ball):

$$M_{chem} = \mu\rho^3 \iint_{\mathbf{R}^3 \times \mathbf{S}^2} \beta(n, S) [u, n] (u, n) \theta((u, n)) f(R - \rho n, p) dn dp. \quad (14)$$

Here  $\mu = \frac{mM}{M+m}$  — is the reduced mass,  $\rho$  is the radius of the ball particle,  $u$  is the relative velocity,  $\theta$  is a Heaviside function.

## 2. System of equation in Maxwell equilibrium for small velocities of a particle.

We take distribution function as Maxwellian.

$$f(t, r, p) = n_0 (2\pi mkT)^{-3/2} \cdot e^{-\frac{|p|^2}{2mkT}}.$$

Assume that the ratio of the particle velocity and the mean square velocity of gas molecules is small.

Then we get the following expressions for integrals (12-14)

$$F_{comp.} = -\frac{8\sqrt{2\pi} \cdot \rho^2 n_0 kT}{3 \cdot (1 + \varepsilon)} \cdot v,$$

$$F_{xem.} = \frac{2\rho^2 n_0 kT}{1 + \varepsilon} \cdot \left\{ -\frac{1 - \varepsilon}{4} \int \beta(n) ndn + \frac{3 - \varepsilon}{2\sqrt{\pi}} \int \beta(n)(v, n) ndn \right\},$$

$$M_{xem.} = -\frac{\rho^3 n_0 kT}{1 + \varepsilon} \sqrt{\frac{2}{\pi}} \cdot \int \beta(n) [v, n] ndn.$$

Here  $v = \frac{Q}{M} \sqrt{\frac{m}{kT}}$  – is a ratio of velocity of a body  $\frac{Q}{M}$  and heat velocity,  $\varepsilon = \frac{m}{M}$  – is a ratio of masses of molecule and a particle.

Let consider  $\beta$  symmetric with respect to rotations around **S**: that means that  $\beta$  is a function of only one variable

$$\beta = \beta((n, S)). \quad (15)$$

Then this system gets the following form.

$$\begin{cases} \frac{dR}{dt} = \frac{Q}{M}, \\ \frac{dQ}{dt} = (\chi_0 + \chi_1 \cdot (Q, S)) \cdot S - \lambda \cdot Q, \\ \frac{dS}{dt} = \frac{1}{J} [K, S], \\ \frac{dK}{dt} = \gamma [Q, S]. \end{cases}$$

Here one has by integrating with Maxwellian and taking in mind (15):

$$\chi_0 = \frac{1 - \varepsilon}{1 + \varepsilon} \pi \rho^2 n_0 kT \int_{-1}^1 \beta(\zeta) \zeta d\zeta,$$

$$\chi_1 = \frac{\rho^2 n_0 \cdot \sqrt{2\pi mkT}}{2M} \cdot \frac{(3 - \varepsilon)}{(1 + \varepsilon)} \cdot \int_{-1}^1 \beta(\zeta) (3\zeta^2 - 1) d\zeta,$$

$$\lambda = \frac{\rho^2 n_0 \cdot \sqrt{2\pi mkT}}{M(1 + \varepsilon)} \cdot \left( \frac{8}{3} - \frac{3 - \varepsilon}{2} \cdot \int_{-1}^1 \beta(\zeta) (1 - \zeta^2) d\zeta \right),$$

$$\gamma = -\frac{\rho^3 n_0 \cdot \sqrt{2\pi mkT}}{M(1 + \varepsilon)} \int_{-1}^1 \beta(\zeta) \zeta d\zeta.$$

Now we shall assume that the rotation is almost constant. Then we get the following system

$$\begin{cases} \frac{dR}{dt} = \frac{Q}{M}, \\ \frac{dQ}{dt} = (\chi_0 + \chi_1(Q, S))S - \lambda Q, \quad \omega = K/J \approx \text{const.} \\ \frac{dS}{dt} = [\omega, S], \end{cases}$$

Integration of this system shows that the trajectory  $R(t)$  tends to cylindrical spiral with a constant step  $L$  and diameter  $D$ :

$$L = \frac{2\pi(P_\infty, \omega)}{M\omega^2}, \quad D = \frac{2\sqrt{P_\infty^2 \omega^2 - (P_\infty, \omega)^2}}{M\omega^2}. \quad (16)$$

The case of general form of a particle was considered by Batisheva [11].

The mechanism of positive and negative photophoresis has to be explained through photoeffect (photoelectric emission). If emission of electron makes photo-sublimation (photodisintegration) we have positive photophoresis. And if it gives photo-adsorption one has negative photophoresis [7]. In both cases photoeffect can be internal (without emission) or external: internal is perhaps more appropriate for explanation of photophoresis.

### 3.Applications.

Chemojet motion is widely spread as we have it for any big particle, chemically or physically reacted with gas. .

So it must have a tremendous number of applications.

Direct and indirect photophoresia have several applications.

It was already discussed for comet astronomy and for possible explanation of forms of Northern Light. A number of applications are considered for planet astronomy in paper of G. Wurm and O. Krauss. [8]. There we also read "One might think of creating an artificial surface with much stronger, optimized photophoretic forces. In analogy to solar sails based on radiation pressure solar sails based on photophoresis could be much stronger. These could, e.g., be used for propulsion of small probes on Mars or in Earth's stratosphere." The idea was independently discussed in [7] in the following words. "Photo-reactive engine. On the basis of direct photophoresis a scheme of *photo-reactive* engine can be proposed. A layer of substance, sublimating under photons, covers a surface of a rocket or some part of it appearing in proper moment. Now they try to construct solar sails and to use irradiation pressure. Reactive forces can help, as they are much stronger. If to use not only photons but other components of solar wind such an engine can be called *Solar-reactive*." It is interesting that in [8] and [7] (and here we follow [5-7]) explanations of direct photophoresis are different. G.Wurm and O Krauss use thermophoresis and solid state Greenhouse effect. So both views from [7] and [8] give complementary pictures. Another application that was discussed in [7] is acceleration of particles by laser beams.

Both indirect and direct photophoresis can be applied for dusty plasma, for Northern lights.

Now it is clear that Felix Ehrenhaft spiral paths and so both positive and negative photophoresia have their explanation in the framework of chemojet motion: former as a consequence of reactive forces and the latter of counter-reactive ones. On the other hand Ehrenhaft spiral paths strongly support all mathematical theory of motion of any big particle in reacting gas (chemojet motion), constructed in papers [9-11].

It is interesting to explain "spiral" path within the path of the larger spiral" – this perhaps could be done by more detailed model.

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